

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083306 A2

- (51) International Patent Classification⁷: **B01J 31/14**, 31/12, 31/22 (74) Agents: **DUNLOP, Alan, J., S. et al.**; Hahn & Hahn Inc., 222 Richard Street, Hatfield, 0083 Pretoria (ZA).
- (21) International Application Number: PCT/ZA02/00064 (81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 12 April 2002 (12.04.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/283,417 12 April 2001 (12.04.2001) US
60/283,419 12 April 2001 (12.04.2001) US
2001/3047 12 April 2001 (12.04.2001) ZA
2001/3049 12 April 2001 (12.04.2001) ZA
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- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/083306 A2

(54) Title: OLIGOMERISATION PROCESS AND CATALYST SYSTEM

(57) Abstract: The invention provides a catalyst system for the oligomerisation of olefins, which catalyst system is prepared from catalyst components selected from the group including at least a chromium source, a substituted phenol, and an organoaluminium compound. The invention further provides an aromatic ether component for a trimerisation catalyst system and an oligomerisation process using said catalyst.

OLIGOMERISATION PROCESS AND CATALYST SYSTEM

Field of the Invention

5 This invention relates to an oligomerisation catalyst system, such as a trimerisation catalyst system for trimerisation of ethylene to 1-hexene, to a method of preparation of said catalyst system, and to a process using said catalyst system.

10 Background to the Invention

The inventors are aware that the oligomerisation of olefins, primarily α -olefins, with chromium catalysts has been extensively studied. More specifically, a number of chromium catalysts have been developed and used to trimerise
15 olefins. In this regard, the trimerisation of ethylene to 1-hexene is significant since, in addition to its use as a specific chemical, 1-hexene is extensively used in polymerisation processes either as a monomer or co monomer. Furthermore, the trimeric products derived from longer chain olefins could be well utilized as synthetic lubricants (e.g. polyalphaolefins / PAO's), as well as various other
20 applications such as components of drilling muds, and as feedstock to prepare detergents and plasticizers.

Known chromium-based processes for the trimerisation of ethylene to 1-hexene include:

25

a) A process disclosed in US Patent No. 4,668,838, in which olefins are trimerised by passing the olefin in contact with a catalyst comprising the reaction product of a chromium compound, an organoaluminium compound hydrolysed with a specific amount of water
30 and a donor ligand selected from hydrocarbyl isonitriles, amines and ethers;

b) European Patent No. 0 416 304 discloses the trimerisation of olefins by chromium-containing compounds, such as, for example, chromium pyrrolides that are prepared by forming a mixture of a chromium salt, a metal amide and an electron pair donor solvent, such as, for example, an ether. These chromium catalysts can be used either unsupported or supported on an inorganic oxide;

c) European Patent No. 0 668 105 discloses a process to trimerise ethylene to 1-hexene comprising contacting ethylene with a stabilized catalyst system comprising a chromium source, a pyrrole-containing compound, a metal alkyl and an aromatic compound;

d) European Patent No. 0 706 983 discloses a process for preparing an α -olefin oligomer which comprises oligomerising an α -olefin in a saturated hydrocarbon solvent in the presence of a chromium-based catalyst system comprising a combination of at least a chromium compound, an amine or metal amide, an alkylaluminium compound and a non-coordinating Lewis acid-containing compound based on an element selected from groups IIIB, IVB, VB and VIB of the periodic table;

e) European Patent No. 0 699 648 discloses a process for producing 1-hexene which comprises trimerising ethylene in a 1-hexene solvent in the presence of a catalyst system obtainable by contacting in a 1-hexene solvent a chromium-containing compound, trialkylaluminium or dialkylaluminium hydride, a pyrrole compound or derivative thereof and a group 13 (III B) or group 14 (IV B) halogen compound;

f) US Patent No. 5,811,618 discloses a process for the trimerisation of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminosilicate and a polydentate phosphine, arsenic and/or stibine coordination complex of a chromium salt, such that 1-hexene is formed; and

g) US Patent No. 6,031, 145 discloses a catalyst system for the oligomerisation of ethylene to 1-butene or 1-hexene where in the catalytic composition is prepared using a pre-prepared chromium compound mixed with a pre-prepared aryloxy aluminium of a specified formula; and a hydrocarbyl aluminium selected from a specified group. This catalyst composition is active at the 0.1 mmol concentration level.

Heterogeneous catalyst systems are often selected over homogeneous catalyst systems due to relative ease of recovering and recycling such catalyst systems. However, the process of trimerisation of ethylene using chromium catalysts supported on an inorganic oxide has problems of insufficient activity, poor selectivity towards the intended trimeric product and leads to unsatisfactory levels of polyethylene by-product.

A catalyst system, a method for preparing the catalyst system, and a process using the catalyst system is proposed with high activity and C6 selectivity for the trimerisation of ethylene to 1-hexene, typically the proposed system comprises a chromium source, a substituted phenol, and an alkyl aluminium compound.

Summary of the Invention

According to a first aspect of the invention there is provided a catalyst system for the oligomerisation of olefins, which catalyst system is prepared from catalyst

components selected from the group including at least a chromium source, a substituted phenol, and an organoaluminium compound.

5 The catalyst system may be a catalyst system for the trimerisation of ethylene to 1-hexene.

The chromium source may be a chromium(III) complex, a chromium (II) or chromium (III) salt, or a chromium salt with a different oxidation number which contains one or more identical or different anions such as halides, carboxylates, and acetylacetonates.

The chromium source may preferably be chromium tris-2-ethylhexanoate.

15 The substituted phenol may be a di-substituted phenol.

The substituted phenol may be a di-aryl-substituted phenol.

The substituents on the phenol may be the same or different, linear or branched, hydrocarbyl groups containing 1 to 30 carbon atoms, for example alkyl, cycloalkyl, alkenyl, aryl, or substituted aralkyl, aryl or cycloalkyl.

The substituted phenol may preferably be 2,6-diphenylphenol.

25 The organoaluminium compound may be an alkyl aluminium compound.

The organoaluminium compound may be in the form Al(R)_3 in which R is a linear or branched hydrocarbyl group having from 1 to 6 carbon atoms.

30 The organoaluminium compound may preferably be triethylaluminium. Also known as TEA.

The abovementioned catalyst system may be prepared by the mixing of the above-mentioned catalyst system components in a suitable solvent

- 5 The catalyst system may include an aromatic ether.

The aromatic ether may be an alkoxy benzene.

The aromatic ether may be a mono alkoxy benzene.

10

The aromatic ether may have the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 carbon atoms. The aryl group may be substituted or unsubstituted.

- 15 Non limiting examples of aromatic ethers useful for the invention include methoxy benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-dimethoxy benzene, dibenzyl ether and diphenyl ether

- 20 The aromatic ether may take the part of a solvent in the catalyst system to which it is added.

The aromatic ether may however act as a co-catalyst, ligand or serve as a stabilizer of any complex formed.

- 25 Magnetic susceptibility measurements using the Evans method (see example 11) indicate that a different catalytic system is formed when an aromatic ether is present than when it is not present.

- 30 The chromium:TEA:substituted phenol ratio may be from 1:10:8 up to 1:40:24, typically 1:20:24.

The invention extends to a process for the trimerisation of ethylene to 1-hexene, said process including contacting an ethylene containing feed under oligomerisation reaction conditions to a catalyst system as described above, said process being carried out in a temperature range of 100°C to 140 °C .

5

The process may be carried out at a temperature of 117°C to 125°C.

The process may be carried out at a temperature of 120°C.

- 10 The process may be carried out at a pressure of above 10 Barg, more specifically above 20 Barg, or even more specifically above 30 Barg.

- 15 The process may be carried out by the introduction of an ethylene feedstock into a reactor with the catalyst system already present in the reactor at a temperature in said temperature range.

The catalyst system may be present in the trimerisation reaction mixture at a concentration of chromium of less than 0.1 mmol, based on elemental chromium.

- 20 The chromium (III) salt, substituted phenol and alkyl aluminium compound may be combined in a mixing container, such as a Schlenk tube, in a suitable solvent. This mixture may then be added to a reactor, such as a Parr reactor, at the appropriate temperature and pressurised with ethylene to form 1-hexene as the reaction product of trimerisation.

25

Alternativley, each component may be added individually to the reactor at the appropriate temperature, in the appropriate solvent and pressurised with ethylene.

The invention extends also to a method of preparing an oligomerization catalyst system substantially as described above, said method including at least the step of contacting in any order in a suitable medium:

- a substituted phenol;
- 5 - an organoaluminium compound; and
- a chromium source.

The suitable medium may be an aromatic ether:

- 10 The aromatic ether may be an alkoxy benzene.

The aromatic ether may be a mono alkoxy benzene.

- 15 The aromatic ether may have the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 carbon atoms. The aryl group may be substituted or unsubstituted.

- Non limiting examples of aromatic ethers useful for the invention include methoxy benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-
20 dimethoxy benzene, dibenzyl ether and diphenyl ether

The aromatic ether may take the part of a solvent in the catalyst system to which it is added.

- 25 The aromatic ether may however act as a co-catalyst, ligand or serve as a stabilizer of any complex formed.

- The chromium source may be a chromium(III) complex, a chromium (II) or chromium (III) salt, a chromium salt with a different oxidation number which
30 contains one or more identical or different anions such as halides, carboxylates, and acetylacetonates.

The chromium source may be chromium tris-2-ethylhexanoate.

The substituted phenol may be a di-substituted phenol.

5

The substituted phenol may be a di-aryl-substituted phenol.

The substituents on the phenol may be the same or different, linear or branched, hydrocarbyl groups containing 1 to 30 carbon atoms, for example alkyl, 10 cycloalkyl, alkenyl, aryl, or substituted aralkyl, aryl or cycloalkyl.

The substituted phenol may be 2,6-diphenylphenol.

15

The organoaluminium compound may be an alkyl aluminium compound.

The organoaluminium compound may be in the form $Al(R)_3$ in which R is a linear or branched hydrocarbyl group having from 1 to 6 carbon atoms.

20

The alkyl aluminium compound may be triethylaluminium, also known as TEA.

The chromium:organoaluminium:substituted phenol ratio may be from 1:10:8 up to 1:40:24, typically 1:20:24.

The catalyst system may be prepared at a temperature selected to be selective 25 for a desired product, for example, 1-hexene.

The invention extends to a homogeneous-ethylene-trimerisation-catalyst-system component, which component includes an aromatic ether having the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 30 carbon atoms.

The component is especially useful for catalyst systems including chromium complexes, substituted phenols and alkyl aluminium compounds

5 The aromatic ether may be an alkoxy benzene.

The aromatic ether may be a mono alkoxy benzene.

Non limiting examples of aromatic ethers useful for the invention include methoxy
10 benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-dimethoxy benzene, dibenzyl ether and diphenyl ether

The component may take the part of a solvent in the catalyst system to which it is added.

15

The component may however act as a co-catalyst, ligand or serve as a stabilizer of any complex formed.

The examples which follow are not intended to limit the invention but rather to
20 show its working by example.

Description of Embodiments of the Invention

Example 1

25

A catalyst system was prepared in a 100 ml Schlenk tube using 0.06 mmol chromium tris-2-ethylhexanoate, 0.87 mmol 2,6-diphenylphenol and 1.2 mmol triethyl aluminium (1.6M in cyclohexane) in 20 ml of anisole. This was added at 130 deg. C to a 300 ml Parr autoclave containing 80 ml of anisole. The reactor
30 was pressurised to 37.5 bar with ethylene, which was fed to the reactor on demand. After 30 minutes the reactor was depressurised, the polymer separated

from the liquid product by filtration, and the liquid product was analysed (GC).
The results are summarised in Table 1

Example 2

5

The reaction was carried out as per Example 1 except that 0.3 mmol of 2,6-diphenylphenol was used with 0.6 mmol triethyl aluminium. The reaction was performed at 130 °C and 50 barg pressure. The results are summarised in Table

1

10

Example 3

The reaction was carried out as per example 2 except that the reactor was pressurised to 25 barg. The results are summarised in Table 1

15

Example 4

The reaction was carried out as per Example 1 except that no 2,6 diphenylphenol was used. The results are summarised in Table 1.

20

Example 5

The reaction was carried out as per example 1 except that xylene was used as solvent instead of anisole. The results are summarised in Table 1.

25

Example 6

The reaction was carried out as per example 5 except that no 2,6-diphenylphenol was included. The results are summarised in Table 1.

30

Example 7

The reaction was carried out as per example 1 except that 4-methylanisole was used as solvent. The results are summarised in Table 1.

Example 8

The reaction was carried out as per example 1 except that 4-bromoanisole was used as solvent. The results are summarised in Table 1.

Example 9

The reaction was carried out as per example 1, except that 1.44 mmol 2,6-di(p-methoxyphenyl)phenol was used as ligand and the reaction was carried out at 120 °C. The results are summarised in Table 1.

Example 10

The reaction was carried out as per example 1, except that 0.87 mmol of 2,6-di(p-tolyl)phenol was used as ligand. The results are summarised in Table 1.

Example 11

The reaction was carried out as per example 1 except that 0.87 mmol of β -Naphthol was used as ligand. The results are summarised in Table 1.

Table 1

Example no.	C6 selectivity (%)	1-hexene selectivity (%)	Mass % polymer	Liquid prod. Activity (g /g Cr/ h)	Total activity (g /g Cr/ h)
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1	89.7	98.9	13.6	19660	22769
2	87.6	97.8	21.5	10226	13033
3	85.1	97.5	11.35	2065	2330
4	53.8	90.7	33	914	1365
5	86.3	94.3	29	5427	7691
6	no reaction				
7	88.9	98.7	22.76	7271	9413
8	No reaction				
9	78.6	98.1	59	1425	3490
10	No reaction				
11	53.8	96.2	55.8	1100	2487

Magnetic susceptibility measurements using Evans¹ method gave the following results for catalyst systems with and without an aromatic ether component.

5

Catalyst System	μ_{eff}
chromium tris-2-ethylhexanoate, 2,6-diphenylphenol, triethylaluminium in xylene	5.2
chromium tris-2-ethylhexanoate, 2,6-diphenylphenol, triethylaluminium in anisole	3.6

The above results indicate that a different catalytic system is formed when an aromatic ether is present.

10 References:

- 1) D.H. Evans: The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance, *J. Chem Soc.*(1959), 2003-2005

Claims

- 5 1. A catalyst system for the oligomerisation of olefins, which catalyst system is prepared from catalyst components selected from the group including at least a chromium source, a substituted phenol, and an organoaluminium compound.
2. A catalyst system as claimed in claim 1, which catalyst system is suitable
10 as an ethylene trimerisation catalyst system.
3. A catalyst system as claimed in any one of the preceding claims, wherein the substituted phenol is a di-substituted phenol.
- 15 4. A catalyst system as claimed in any one of the preceding claims, wherein the substituted phenol is a di-aryl-substituted phenol.
5. A catalyst system as claimed in any one of the preceding claims, wherein the substituents on the phenol are linear or branched hydrocarbon groups
20 containing 1 to 30 carbon atoms.
6. A catalyst system as claimed in any one of the preceding claims, wherein the organoaluminium compound is an alkyl aluminium compound.
- 25 7. A catalyst system as claimed in any one of the preceding claims, wherein the organoaluminium compound is in the form Al(R)_3 in which R is a linear or branched hydrocarbyl group having from 1 to 6 carbon atoms.
8. A catalyst system as claimed in any one of the preceding claims, wherein
30 the substituted phenol is 2,6-diphenylphenol.

9. A catalyst system as claimed in any one of the preceding claims, wherein the organoaluminium compound is an alkyl aluminium compound.

10. A catalyst system as claimed in claim 9, wherein the alkyl aluminium compound is triethylaluminium (TEA).

11. A catalyst system as claimed in any one of the preceding claims, including an aromatic ether.

12. A catalyst system as claimed in claim 11, wherein the aromatic ether is an alkoxy benzene.

13. A catalyst system as claimed in claim 11 or claim 12, wherein the aromatic ether is a mono alkoxy benzene.

14. A catalyst system as claimed in claim 11, wherein the aromatic ether has the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 carbon atoms.

15. A catalyst system as claimed in any one of claims 11 to 14, wherein the aromatic ether is selected from one or more of the group including at least methoxy benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-dimethoxy benzene, dibenzyl ether, and diphenyl ether

16. A catalyst system as claimed in any one of claims 10 to 15, having a chromium:TEA:substituted phenol ratio from 1:10:8 up to 1:40:24.

17. A catalyst system as claimed in claim 16, having a chromium:TEA:substituted phenol ratio of 1:20:24.

18. A process for the trimerisation of ethylene to 1-hexene, said process including the contacting of an ethylene containing stream under oligomerisation reaction conditions with a catalyst system which is prepared from catalyst components selected from the group including at least a chromium source, a substituted phenol, and an organoaluminium compound, said process being carried out in a desired temperature range of 100°C to 140 °C
19. A process as claimed in claim 18, wherein the catalyst components from which the catalyst system is prepared include an aromatic ether.
20. A process as claimed in claim 19, wherein the process is carried out at a temperature of 117°C to 125°C.
21. A process as claimed in claim 20, wherein the process is carried out at a temperature of 120°C.
22. A process as claimed in any one of claims 18 to 20, which is carried out at a pressure of above 10 Barg.
23. A process as claimed in any one of claims 18 to 22, which is carried out at a pressure of above 20 Barg.
24. A process as claimed in claim 23, which is carried out at a pressure of above 30 Barg.
25. A process as claimed in any one of claims 18 to 24, in which the catalyst system is present at an elemental chromium concentration, of less than 0.1 mmol/100ml.
26. A process as claimed in any one of claims 18 to 25, wherein the process is performed by the introduction of an ethylene feedstock into a reactor with the

catalyst system already present in the reactor at a temperature in the temperature range of 100°C to 140°C.

27. A method of preparing an oligomerization catalyst system, said method including at least the step of contacting in any order, in a suitable medium:

- a substituted phenol;
- an organoaluminium compound; and
- a chromium source.

28. A method as claimed in claim 27, wherein the suitable medium is an aromatic ether.

29. A method as claimed in claim 28, wherein the aromatic ether is an alkoxy benzene.

30. A method as claimed in claim 28 or claim 29, wherein the aromatic ether is a mono alkoxy benzene.

31. A method as claimed in claim 28, wherein the aromatic ether has the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 carbon atoms.

32. A method as claimed in any one of claims 28 to 31, wherein the aromatic ether is selected from one or more of the group including at least methoxy benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-dimethoxy benzene, dibenzyl ether, and diphenyl ether

33. A method as claimed in any one of claims 27 to 32, wherein the chromium:organoaluminium compound:substituted phenol ratio is from 1:10:8 up to 1:40:24, typically 1:20:24.

34. A method as claimed in any one of claims 27 to 33, wherein the organoaluminium compound is an alkyl aluminium compound.
35. A method as claimed in claim 34, wherein the alkyl aluminium compound
5 is triethylaluminium (TEA).
36. A method as claimed in any one of claims 27 to 35, wherein the substituted phenol is 2,6-diphenyl phenol.
- 10 37. A homogeneous ethylene trimerisation catalyst system component, which component includes an aromatic ether having the formula Aryl-O-R, in which R is a linear or branched hydrocarbyl radical having 1 to 6 carbon atoms.
38. A homogeneous ethylene trimerisation catalyst system component, as
15 claimed in claim 37, wherein the aromatic ether is an alkoxy benzene.
39. A homogeneous ethylene trimerisation catalyst system component, as claimed in claim 37 or claim 38, wherein the aromatic ether is a mono alkoxy benzene.
20
40. A homogeneous ethylene trimerisation catalyst system component, as claimed in any one of claims 37 to 39, wherein the aromatic ether is selected from the group including methoxy benzene (anisole), 1,2-dimethoxy benzene, 1,3-dimethoxybenzene, 1,4-dimethoxy benzene, dibenzyl ether, and diphenyl
25 ether

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Time Printed: 11:31:22 AM

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 August 2002 (29.08.2002)

PCT

(10) International Publication Number
WO 02/066405 A1

(51) International Patent Classification⁷: **C07C 2/32, B01J 31/22**

(21) International Application Number: **PCT/NL02/00119**

(22) International Filing Date: 22 February 2002 (22.02.2002)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
PCT/NL01/00149

22 February 2001 (22.02.2001) **NL**

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(48) Date of publication of this corrected version:

2 October 2003

(15) Information about Correction:

see PCT Gazette No. 40/2003 of 2 October 2003, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/066405 A1

(54) Title: **CATALYST SYSTEM FOR THE TRIMERISATION OF OLEFINS**

(57) Abstract: The invention relates to a catalyst system for the selective trimerisation of olefins, which system is based on a titanium complex of formula $(Cp-B(R)_nAr)TiR^1_3$, wherein: Cp is a cyclopentadienyl type ligand, optionally substituted, B is a bridging group, based on a single atom selected from the groups 13 to 16 inclusive of the Periodic System, Ar is a aromatic group, optionally substituted, R is, independently, hydrogen, or a hydrocarbon residue, optionally being substituted and optionally containing heteroatoms, or groups R and B are joined together to form a ring, n is an integer equal to the (valency of B minus 2), and R¹ is a mono-anionic group, and further comprises an activator. The present catalyst system obviates the use of toxic chromium compounds.